June 21, 2002

Annual Progress Report

Project Title: The Carbonate System in Florida Bay
Grantee: Dr. Frank J. Millero
Award Period: From 08/01/00 to 07/31/02
Period Covered by this Report: 08/01/00 to 07/31/02
Summary of Progress:

1. Work Accomplishments

For the last four years, we have been studying the carbonate system in Florida Bay. These studies include measurements of pH, total alkalinity (TA), total inorganic carbon dioxide (TCO_2) and the partial pressure of CO_2 (pCO_2) of waters in the bay and surrounding waters. The results of this study have shown that carbonate is added to the waters flowing into the bay through Taylor Slough along with phosphate. The increased carbonate concentration results from the low pH of the waters in the Mangrove fringe due to the oxidation of organic carbon. For the western basin in the summer, our measurements indicate that $CaCO_3$ is precipitated from the high salinity waters. Measurements of pCO_2 in the Fall show a "pull down" of 40 μatm due to primary production (relative to the atmosphere) (Millero et al., 2000). Over the last two years, we have continued our studies of the carbonate system in Florida Bay and surrounding waters.

Over the last two years, we have studied the composition of the sediments and pore waters. These include studies of the organic carbon and nitrogen; the Ca, Mg and trace metals (Fe, Mn, Cu, Hg, etc.) in the sediments.

All of our fieldwork has been coordinated with Dr. Peter Ortner (AOML/NOAA) and Dr. Thomas Lee (RSMAS/UM). Over the last six years, Dr. Ortner's group has provided us with samples collected in the bay at 40 sites. Carbonate measurements were made on these samples from 1997 to 2002. Sediment samples were collected in Florida Bay and adjacent waters over the last two years.

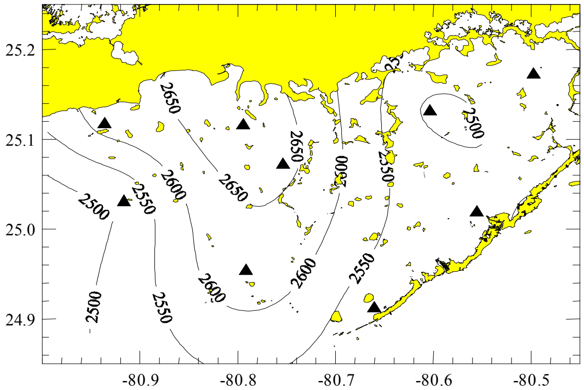
A number of cruises in waters surrounding the bay, including the Florida Straits and Gulf of Mexico, have examined nutrients, carbonate parameters and trace metals. These measurements have been used to fully characterize and compare the chemistry of Florida Bay and the surrounding waters.

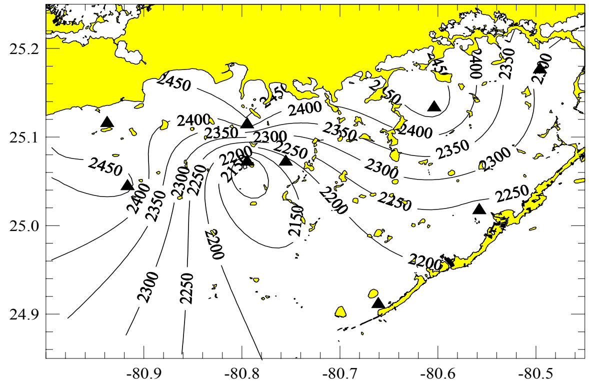
A close examination of the CO_2 parameters throughout the year show that the lowest pCO_2 occurs in the western part of the Bay in July in a region that also has the highest levels of Chlorophyll (**Figure 1 and Figure 2**). This could be the result of the pulldown of CO_2 during primary production in the bay. The TA and TCO_2 levels do not appear to be affected by this production possibly due to the carbonate buffering capacity.

Fig. 1 pCO_2 (μatm) contours in Florida Bay

Fig. 2 Chlorophyll (μg L^{-1}) contours in Florida Bay

Contour plots of TA for two months are shown in **Fig. 3 and 4**. The TA and



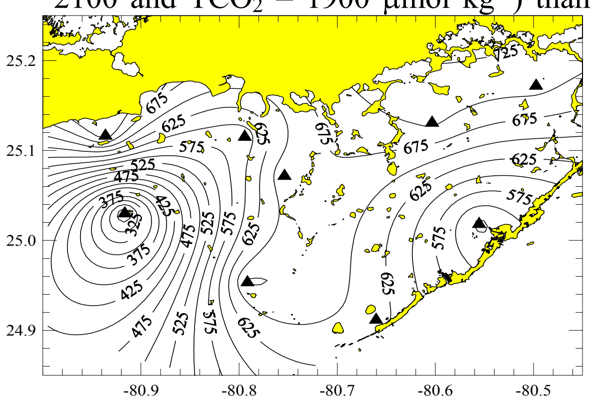


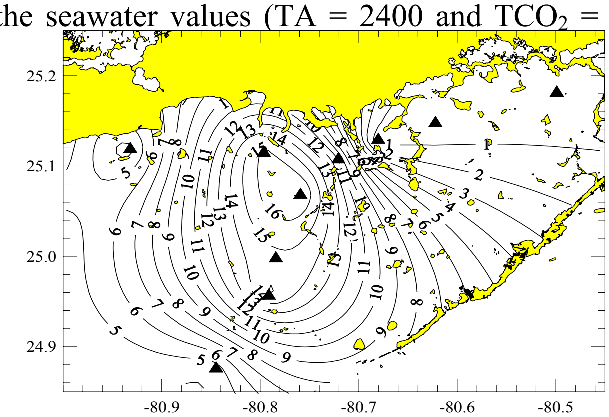
TCO_2 of the input waters are much higher than seawater due to the high pH and low aragonite and calcite saturation states of these waters. Their low pH results in the high values of TA in these waters due to the dissolution of $CaCO_3$. During the

Fig. 3 TA (μmol kg^{-1}) contours – Winter

Fig. 4 TA(μmol kg^{-1}) contours– Spring

summer when the salinity is the highest, the values of TA and TCO_2 are lower (TA = 2100 and TCO_2 = 1900 μmol kg^{-1}) than the seawater values (TA = 2400 and TCO_2 =





2100 μmol kg^{-1} when S = 35). This is due to the precipitation of $CaCO_3$ in these waters. This precipitation can be caused by inorganic precipitation due to the mixing of sediments with the high salinity waters or the formation of biogenic $CaCO_3$ by macroalgae.

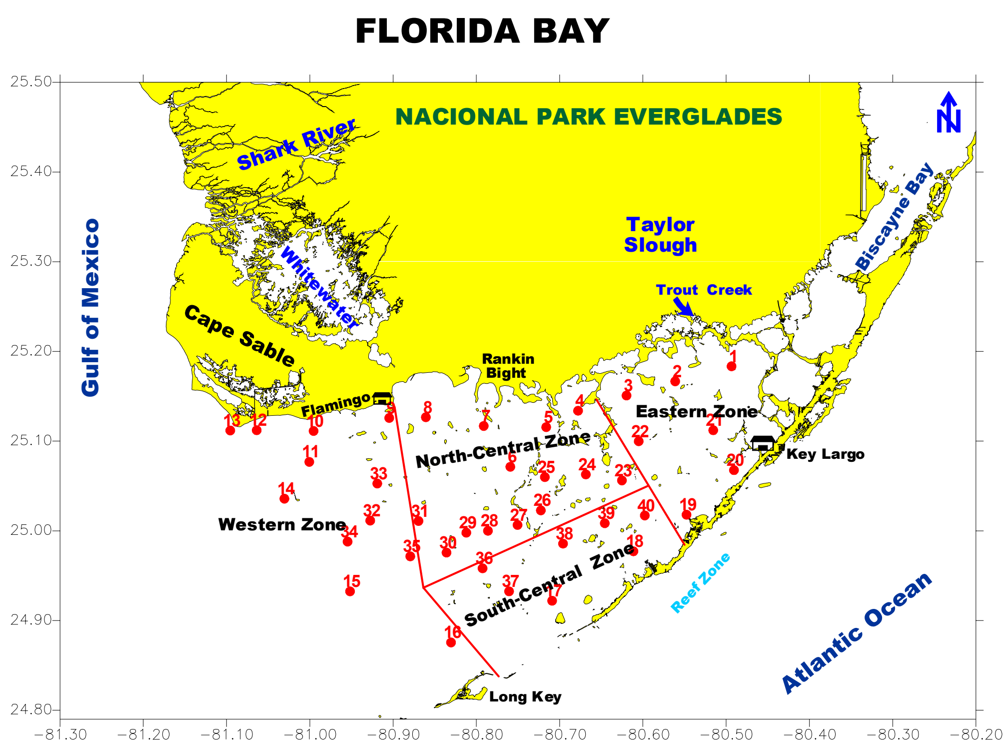
The general features of the carbonate system in the bay are similar to studies made on estuarine waters entering from the western part of the everglades. For example, measurements made in the Shark River yield high values of TA (3500 μmol kg^{-1}), TCO_2 (3000 μmol kg^{-1}), and pCO_2 (1000 μatm) and low values of pH (7.9). As stated earlier, we feel that these large increases of CO_2 are related to photochemical and biological oxidation.

The high values of TA for the input waters along the mangrove fringe are due to their low pH, which results in the dissolution of $CaCO_3$. Changes in salinity, phosphate concentration, total alkalinity and pH occur as the freshwater input from Taylor Slough travels across the mangrove fringe. The low pH of the freshwater end member, that is responsible for the high total alkalinity values, also leads to an increase in phosphate concentration along the mangrove fringe. Increase phosphate concentrations are due to the desorption of phosphate as the calcium carbonate mineral is dissolved. Calcium carbonate has a high affinity for phosphate adsorption; conversely during desorption the phosphate can be very easily released from calcium carbonate back to the solution.

The Trace Metals in the Sediments of Florida Bay

During the last two years, we have concentrated on the analysis of metals in the sediments of Florida Bay. We sampled surface sediments for 3 months (June 00, November 00 and February 01) at 40 stations shown in **Figure 1.** The stations were selected to represent the various zones of the Bay. The samples were collected by taking

Figure 1. The stations sampled in Florida Bay and the various zones.



the inside of a grab sample of the surface sediments. Care was taken to store the sediments in pre-cleaned HDPE (high density polyethylene) bottles that were frozen until analysis. The samples were defrosted in the laboratory and dried under a clean laminar flowing bench for two days. The dry sediment (0.8 g) was digested with HNO_3 in Teflon tubes. The sample was centrifuged and filtered through an acid-cleaned 0.45µm Supor Acrodisc Gelman filter. The metals in the filtrate were analyzed using an inductive coupled plasma mass spectrophotometer (ICP-MS). The samples for Sc, V, Ba, Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn were diluted by 1:20 and for Al and Mg 1:1000 (V. Gonzalez-

Caccia, F.J. Millero, and A. Palanques, in preparation). The concentration of Fe in the sediments was determined by the Ferrozine method (Stookey, 1970).

Organic carbon and nitrogen was also measured in the sediments as well as Ca and Mg. The values of organic carbon and calcite in the sediments are shown in **Figures 2 and 3**. The sediments are predominately $CaCO_3$ as found by other workers (Ginsburg, 1956; Stockman et al., 1967; Bosence, 1989).

Figure 2. The percent of Organic Carbon in Sediments from Florida Bay (Nov 00)

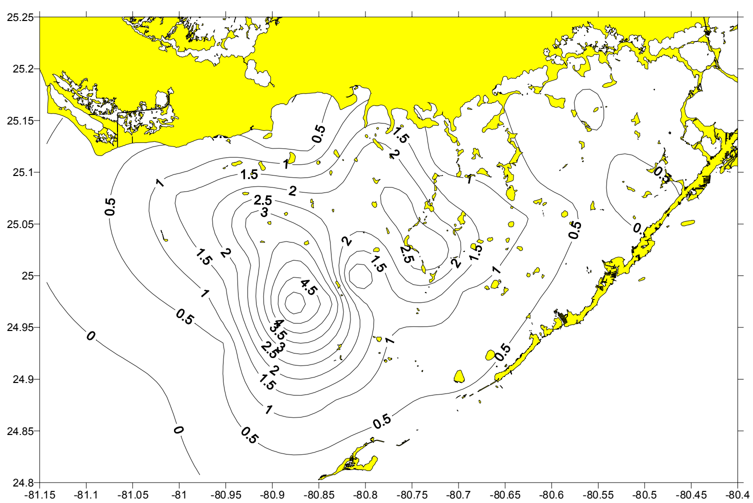
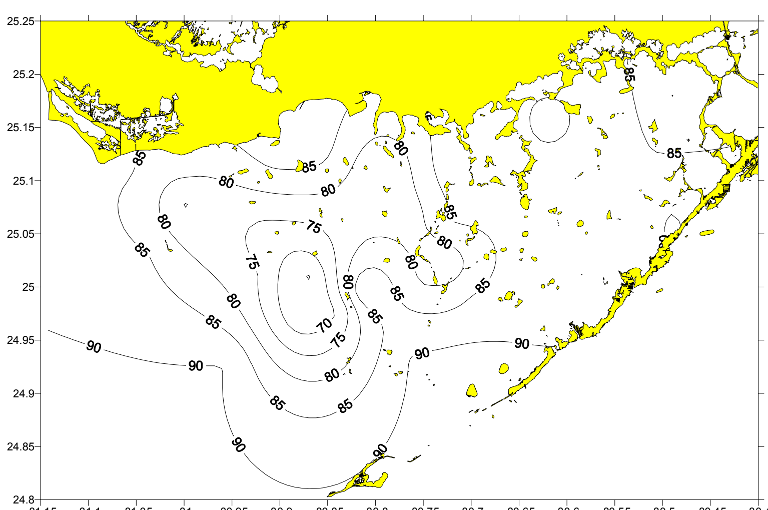


Figure 3. The percentage of $CaCO_3$ in Sediments from Florida Bay (Nov 00)



The organic carbon content in the Florida Bay surface sediments varied from 0 % to 5.5 % and the percent of $CaCO_3$ varied between 65.9 % to 92.5 %. The highest value of organic carbon (5.5%) and the lowest value of $CaCO_3$ (65.9%) were found in the western zone.

The complete measurements made on the sediments (120 samples) are given elsewhere (Gonzalez-Caccia, 2002; Gonzalez-Caccia et al., 2002). The metals in the sediments for the various months studied show a similar pattern. Some typical results are shown in **Figures 4 and 5** for Cu and Mn. The maximum concentrations of Al, Co, Ni, V, Mg, Zn, Cu, Cr, Pb, Ba, Sc were observed in the north-central zone and western zone. This distribution pattern is similar to the organic carbon in the sediments. A number of the metals (Al, Mg, Cr, Pb, Zn, Mn and Fe) exhibited high concentrations in the northern part of the Eastern Zone. Mg, Cr, Pb show this pattern only in the winter months, November and February, but not in June. The concentrations of Zn, Mn and Fe were the same for all three months. Ni, Mg, Cr, Ba, Zn, Cu and Pb also showed high concentrations at station 19 in June 00 and February 01. This could be related to boat traffic near the marina at Tavernier Creek.

Figure 4. The concentration of Cu [nM/g] in Sediments from Florida Bay (June 00)

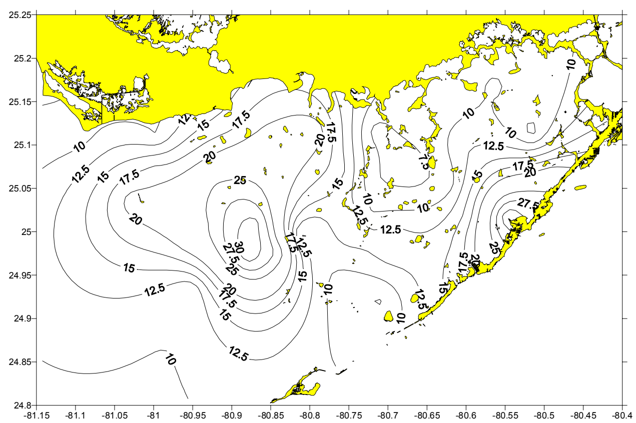
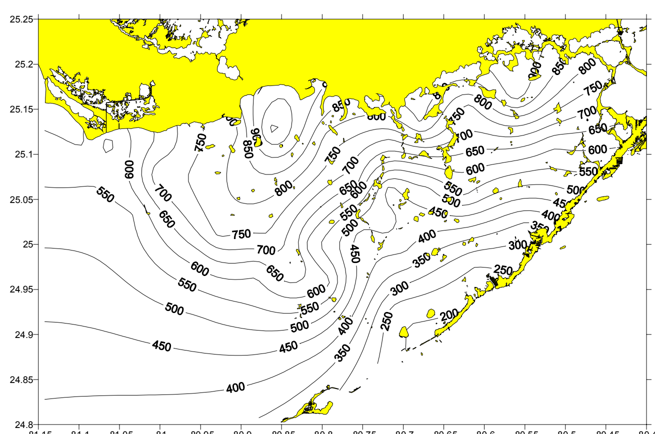
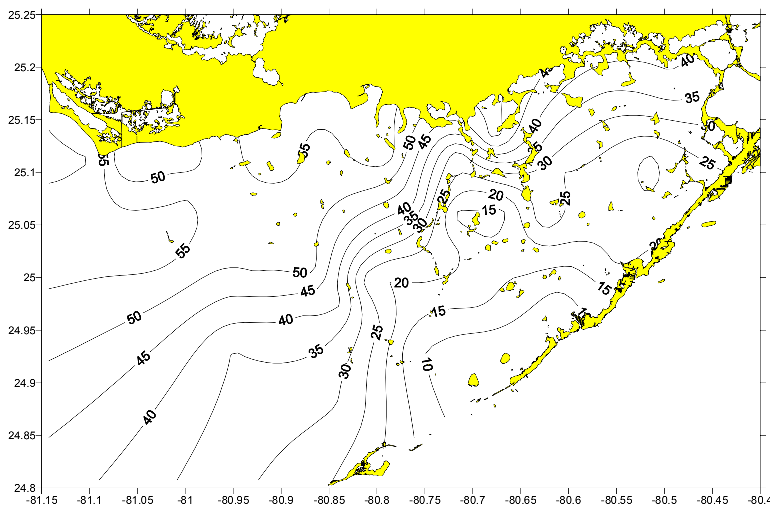


Figure 5. The concentration of Mn [nM/g] in Sediments from Florida Bay (Feb 01)



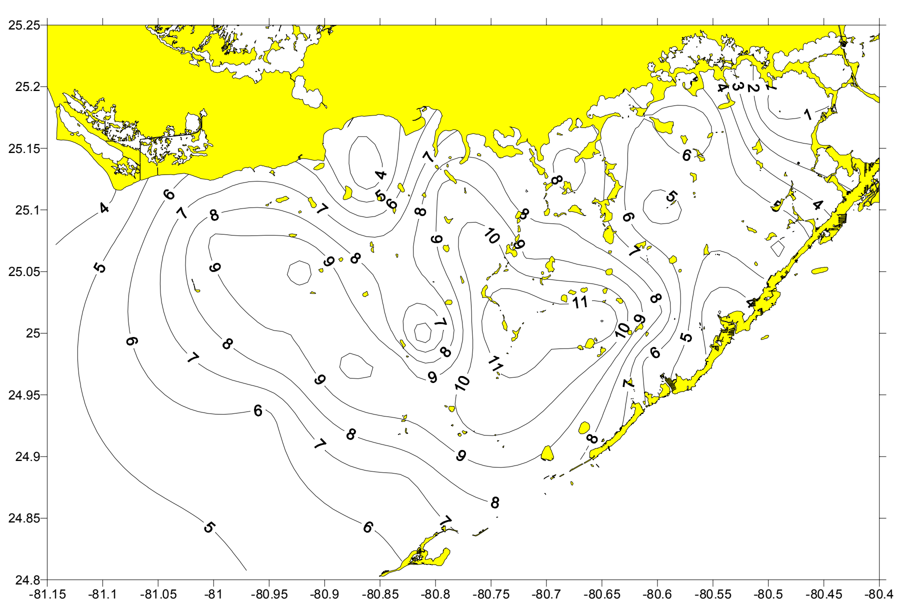
Mn and Fe distributions were different than other metals. Their concentrations gradually decreased from the North (Everglades) to the South (Florida Keys). In the case of Fe, we also note a strong contribution or input that comes from the Western part of the Bay (stations 11 and 13) **(Figure 6)**, and in the case of Mn the maximum values appear to come from Rankin Bight (station 8) **(Figure 5)**. These high values could be attributed to the continental input and runoff from the creeks of Taylor Slough and Shark River. The south central zone exhibited the minimum concentrations of all metals in sediments and the lowest concentrations were found at station 17. This zone is exactly located near the Key Channels, which exchange waters from the Atlantic and Gulf Stream that contain very low concentrations of trace metals. For this reason, we can explain the low concentrations in this zone.

Figure 6. The concentration of Fe [µM/g] in Sediments from Florida Bay (June 00)



The distribution pattern of many of the metals was similar to the distribution of organic carbon with maximum concentrations in the North-Central and Western Zones. The C/N also exhibited the same distribution pattern as the organic carbon (**Figure 7**).

Figure 7. The distribution of C/N in Sediments from Florida Bay (Nov 00)



The maximum C/N (9-12) was observed in the stations with the highest organic carbon where there are dense colonies of seagrass**.** Lutz (1997) has done extensive research on the origin of organic carbon in Florida Bay using C/N and $\delta^{13}C$. He suggests that the dominant marine source of organic carbon comes from seagrasses with a lesser amount from phytoplankton. The most common values of C/N for seagrasses (mainly Thalassia) is 11, for phytoplankton between 5 to 6 and for mangroves >20 (Lutz, 1997). Our distribution patterns of %OC and C/N are in agreement with his results. Also our results of DOC (Gonzalez-Caccia, 2002) show a similar distribution pattern with the OC **(Figure 8)**. The maximum concentration of DOC comes from the northern coast (Everglades) around Rankin Bight. This zone is also where phytoplankton blooms occur as shown by inorganic carbon data (Millero et al., 2000) and where one finds the highest values of pH **(Figure 9)**.

Figure 8. The distribution of dissolved organic carbon DOC [µMol] in Seawater from Florida Bay (May 01)

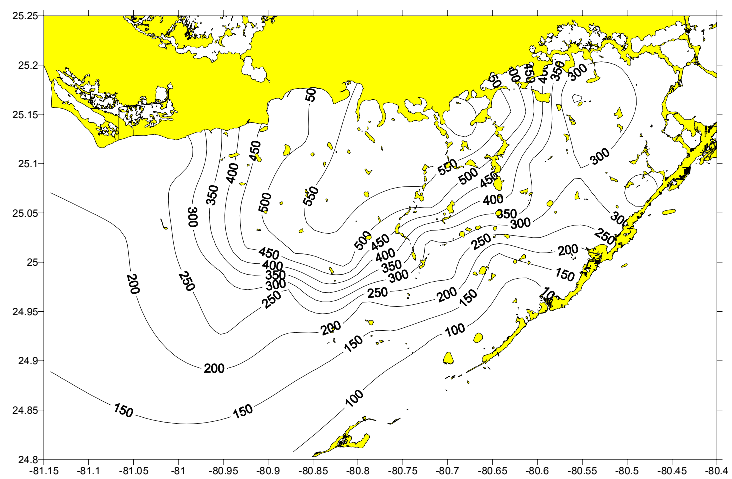
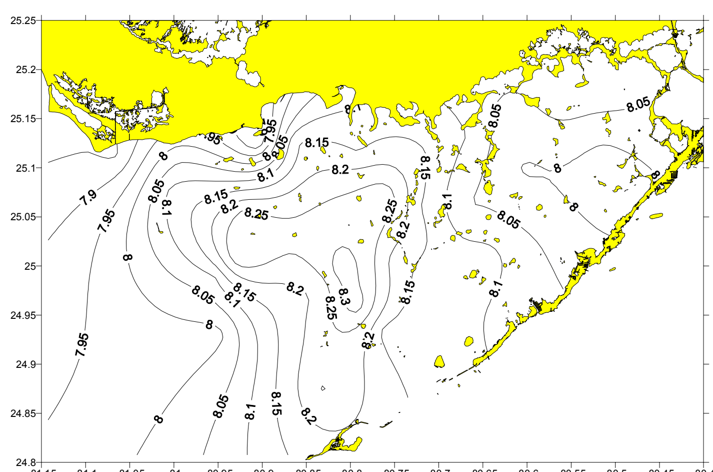


Figure 9. The distribution of pH in Seawater from Florida Bay (May 01)



The direct correlation between high concentrations of metals, high percent of organic carbon and C/N, also is related with the bottom type. We have found that the stations with high concentrations of metals and organic carbon are localized in seagrass bottoms and open mud. Prager & Halley (1999) classified the bottom types in Florida Bay, finding the dense to intermediate beds of seagrass, mainly *Thalassia testudinum* in the shallow basins of western Florida Bay and the open mud at the north of the north-central zone and western zone. They observed the highest organic carbon content in these two bottom types. Wave measurements and modeling indicate that *Thalassia* along mud bank margins can reduce incoming wave energy by over 80%. For this reason sea grasses play a vital role in mud bank formation and stability in Florida Bay, and in the production of carbonate sediments. In the eastern and south-central zone, they found that extensive areas with mainly hard bottoms contain the highest percent of $CaCO_3$ and the lowest percent of organic carbon. These zones have lower concentrations of metals.

Wanless & Taggett (1989) classified Florida Bay into four areas according to its bank morphology, internal stratigraphy, bank dynamics, sediment supply, physical processes and biogenic communities: 1) *Inner Destructional Zone* in the eastern side (this zone is sediment starved), 2) *Central Migration Zone* in the center of the bay (this zone receives sufficient sediment supply to maintain banks), 3) *Western Constructional Zone* in the western side (it has very broad and actively expanding banks), because of its proximity to more marine waters, sediment production appears to be more rapid and excess sediment from local production and detrital input has caused bank growth, and 4) *Outer Destructional Zone* along the exposed western margin of Florida Bay (Wanless & Taggett, 1989). We notice that low concentrations of metals are related to the destructional zones and high concentrations of metals are related to the constructional zones. One explanation is that both Shark River and Taylor Slough maybe the source of these metals either in the dissolved or particulate form. The sea grass beds with high organic content might trap them.

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2. Applications

The results of this project are posted online (http://www.rsmas.miami.edu /groups/jmc/fla-bay/fbay.html. All 17 parameters (Temperature, Salinity, Total Alkalinity, Normalized Total Alkalinity, Total Carbon Dioxide, Normalized Total Carbon Dioxide, Chlorophyll, Calcite, Aragonite, pH, partial pressure of Carbon Dioxide, NH_4, NO_2, NO_3, NO_2&NO_3, SiO_2, and PO_4) are updated regularly. The data and figures are free for all scientific parties as long as the PI and Funding Agency are mentioned when they are used. Our results were also published in the *Bulletin of Marine Science*, Vol. 68(1): 101-123,2001. Three people (Dr. Millero, William Hiscock and Valentina Caccia) from our group participated in the 2001 Florida Bay Science Conference at Westin Beach Resort, Key Largo, Florida. April 23-26, 2001. Two presentations were posted on the conference: One named the Seasonal Variation on the Carbonate System in Florida Bay with the authors of William Hiscock and Frank Millero; and One named Trace metals in Florida Bay with authors Frank Millero, Valentina Caccia at the University of Miami and Xuewu Liu at University of South Florida, St. Petersburg, Florida. The contents of these two presentations will be submitted to the journals, *Marine Chemistry* and *Marine Pollution Bulletin*. In addition Valentina Gonzalez-Caccia will defend her PhD. Dissertation this fall at the University of Catalunya, Barcelona, Spain.

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